The following notice applies to any unclassified (including originally classified and now declassified) technical reports released to "qualified U.S. contractors" under the provisions of DoD Directive 5230.25, Withholding of Unclassified Technical Data From Public Disclosure.

NOTICE TO ACCOMPANY THE DISSEMINATION OF EXPORT-CONTROLLED TECHNICAL DATA

1. Export of information contained herein, which includes, in some circumstances, release to foreign nationals within the United States, without first obtaining approval or license from the Department of State for items controlled by the International Traffic in Arms Regulations (ITAR), or the Department of Commerce for items controlled by the Export Administration Regulations (EAR), may constitute a violation of law.

2. Under 22 U.S.C. 2778 the penalty for unlawful export of items or information controlled under the ITAR is up to ten years imprisonment, or a fine of $1,000,000, or both. Under 50 U.S.C., Appendix 2410, the penalty for unlawful export of items or information controlled under the EAR is a fine of up to $1,000,000, or five times the value of the exports, whichever is greater; or for an individual, imprisonment of up to 10 years, or a fine of up to $250,000, or both.

3. In accordance with your certification that establishes you as a "qualified U.S. Contractor", unauthorized dissemination of this information is prohibited and may result in disqualification as a qualified U.S. contractor, and may be considered in determining your eligibility for future contracts with the Department of Defense.

4. The U.S. Government assumes no liability for direct patent infringement, or contributory patent infringement or misuse of technical data.

5. The U.S. Government does not warrant the adequacy, accuracy, currency, or completeness of the technical data.

6. The U.S. Government assumes no liability for loss, damage, or injury resulting from manufacture or use for any purpose of any product, article, system, or material involving reliance upon any or all technical data furnished in response to the request for technical data.

7. If the technical data furnished by the Government will be used for commercial manufacturing or other profit potential, a license for such use may be necessary. Any payments made in support of the request for data do not include or involve any license rights.

8. A copy of this notice shall be provided with any partial or complete reproduction of these data that are provided to qualified U.S. contractors.

DESTRUCTION NOTICE

For classified documents, follow the procedure in DoD 5220.22-M, National Industrial Security Program, Operating Manual, Chapter 5, Section 7, or DoD 5200.1-R, Information Security Program Regulation, Chapter 6, Section 7. For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
26 May 2016	Briefing Charts	29 April 2016 – 26 May 2016

4. TITLE AND SUBTITLE
Balancing Performance and Sustainability in Next-Generation PMR Technologies for OMC Structures (Briefing Charts)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Gregory R. Yandek, Jason T. Lamb

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q16J

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd
Edwards AFB, CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB, CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2016-110

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited. PA Case Number: #16223; Clearance Date: 5/6/2016

13. SUPPLEMENTARY NOTES
For presentation at Society for the Advancement of Materials and Process Engineering; Long Beach, CA, USA (May 26, 2016)
See also AD1010456, Accompanying Technical Paper AFRL-RQ-ED-TP-2016-107

14. ABSTRACT
Viewgraph/Briefing Charts

15. SUBJECT TERMS
N/A

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			A Guenthner
Unclassified	**Unclassified**	**Unclassified**	SAR	36	**19b. TELEPHONE NO** *(include area code)* N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Balancing Performance and Sustainability in Next-Generation PMR Technologies for OMC Structures

Gregory R. Yandek,[1] Jason T. Lamb,[2] John J. La Scala,[3] Benjamin G. Harvey,[4] Giuseppe R. Palmese,[5] William S. Eck,[6] Joshua M. Sadler,[3] Santosh K. Yadav[5]

Air Force Research Laboratory, Rocket Propulsion Division[1], ERC, Inc.[2], Edwards AFB, CA
U.S. Army Research Laboratory, Weapons & Materials Research Directorate[3], Aberdeen Proving Ground, MD
Naval Air Warfare Center, Weapons Division[4], China Lake, CA
Drexel University, Department of Chemical and Biological Engineering[5], Philadelphia, PA
U.S. Army Public Health Center[6,] Aberdeen Proving Ground, MD

26 May 2016

WP-2402: Novel Chemistries for Replacement of Methylenedianiline in Polyimide Composites

Performers:

- *J. La Scala, J. Sadler, Army Research Laboratory; B. Harvey, Naval Airfare Warfare Center; G. Palmese, Drexel U.; G. Yandek, Air Force Research Laboratory; W. Eck, Army Public Health Center*

Technology Focus

- *Develop sustainable high temperature polyimide resins for high performance DoD applications by systematically exploring polymer/composite properties and toxicity of structural variants of MDA using renewable and petroleum-derived chemicals.*

Research Objectives

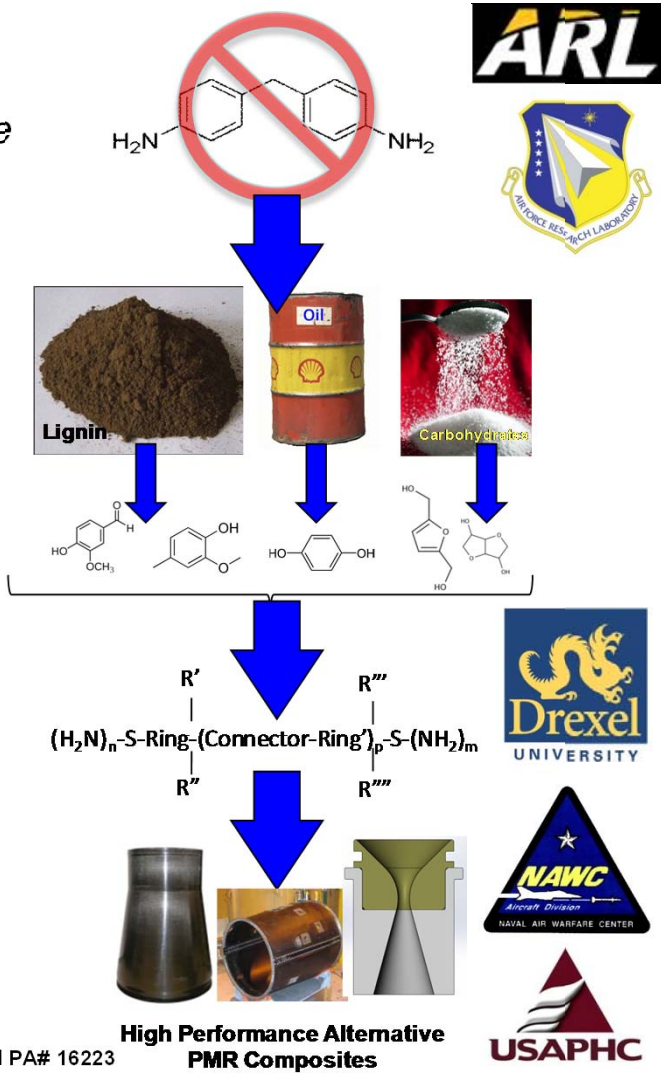
- *Develop structure-property-toxicity relationships of MDA alternatives.*

Project Progress and Results

- *Identified lower toxicity diamines with low toxicity, good processing, and good polymer properties.*
- *Identified a few gaps in structure-property-toxicity understanding.*

Technology Transition

- *Transition to Polyimide pre-preg manufacturers and rocket manufacturing primes. Transition to AF and Army high temperature composites programs.*



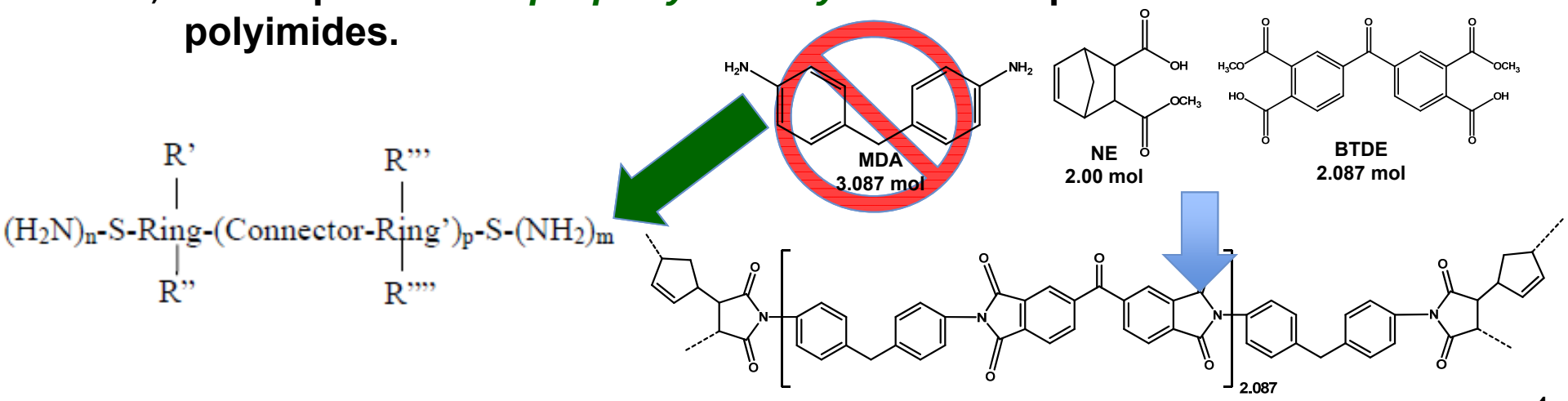
Performers

Org.	Team Members	Activities
ARL	Dr. J.J. La Scala (PI) Dr. J. Sadler Dr. C. Paquette Ms. R. Toulan Mr. C. Annunziato Dr. I. McAninch	PI Duties. Chemical preparation and analysis of furan-based and other MDA replacements. Polyimide resin preparation and characterization. Environmental and cost assessment
NAWC	Dr. B. Harvey (co-PI) Dr. M. Garrison Dr. M. Davis Dr. A. Chafin Dr. M. Savolainen	Chemical preparation and analysis of lignin-based and other MDA replacements. Polyimide resin preparation and characterization.
Drexel University	Dr. G.R. Palmese (Co-PI) Mr. F. Hu Dr. S. Yadav	Chemical preparation and analysis of furan-based and other MDA replacements. Polyimide resin preparation and characterization.
AFRL	Dr. G. Yandek (co-PI) Dr. J. Lamb	Pre-preg and composite preparation and characterization.
Army Public Health Center	Dr. W. Eck (co-PI) Dr. V. Adams Dr. C. Cao	QSAR Analysis and Toxicity studies of relevant chemicals and polymers.

Technical Objective

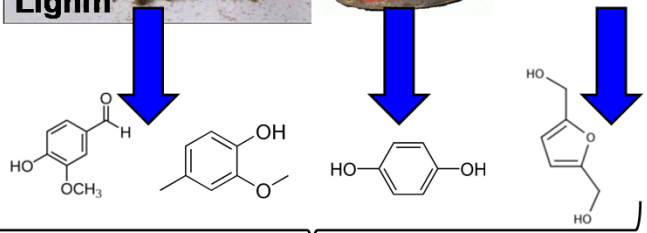
Develop novel chemistries utilizing polymer, health, and environmental sciences to replace MDA in PMR polyimides for high temp composites with both petroleum-derived and renewable/bio-derived monomers that achieve the following:

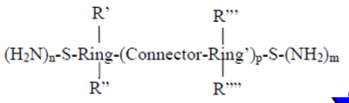
1) **Reduce/eliminate toxicity and carcinogenic aspects of the polyimide**
2) **Maintain thermal and mechanical properties of the composites**
3) **Simplify composite processing**
4) **Reduce lifecycle costs**
5) **Develop *structure-property-toxicity* relationships of these novel polyimides.**



Technical Approach

Carbohydrates

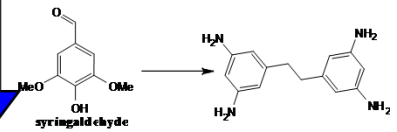




Task 1: QSAR Analysis

Non-Toxic MDA Alternative Structures Identified

Task 2: Chemistry



MDA Alternatives Synthesized

Task 3: Monomer and Resin Processing

MDA-Free PMR is Processable for Pre-Preg

Task 4: Polymer Properties

High Performance PMR Alternative

Task 5: Toxicology Analysis

Demonstrate Reduced Toxicity of MDA/PMR Alternative

Subtask 6.1: Composite Properties

High Performance Alternative PMR Composites

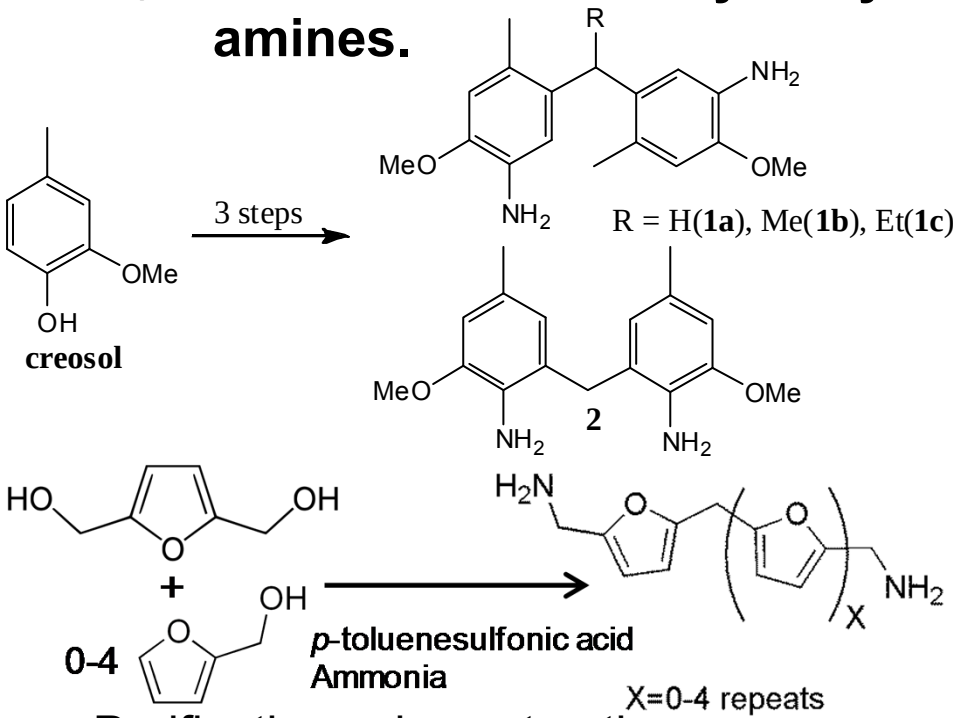
Subtask 6.2: Composites Demonstration

Task 7: Life Cycle Analysis

Demonstrated Alternative PMR Composites

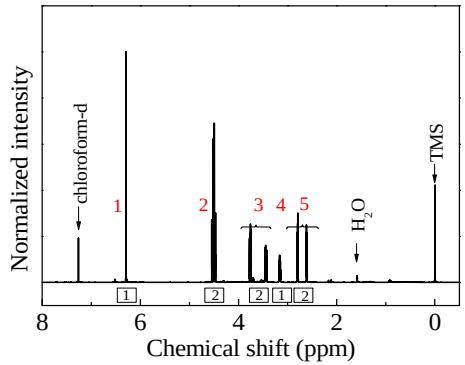
Chemistry to Prepare MDA Alternatives

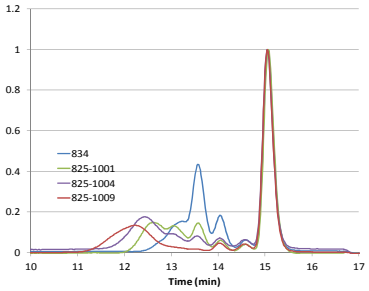
- **Various potential rxn schemes.**
  1) **Joining of two hydroxyl containing chemicals**
  2) **Conversion of the hydroxyls to amines.**



Purification using extraction, crystallization, and distillation.

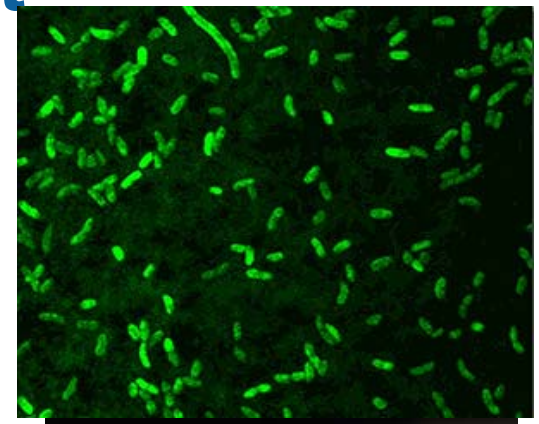
- **Analytical chemistry of products**
  - **NMR, FTIR – chemical analysis**
  - **SEC – Molecular weight analysis**

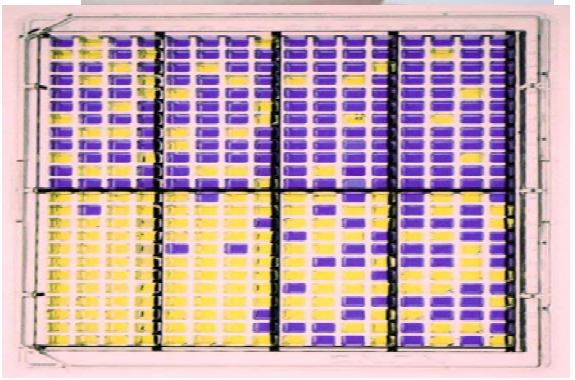




Toxicology Assessment

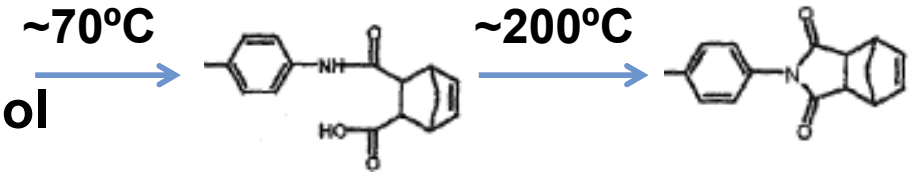
- **Quantitative Structure-Activity Relationship (QSAR) principle –predict properties based on chemical structure**
  - **EPA's EPI Suite model package – physical properties**
  - **TOPKAT – human toxicity prediction**
  - **ECOTOX modeling system – Environmental toxicity**
- ***in vitro* testing**
  - **Performed on bacterial cells (e.g. *S. typhimurium* and *E. coli*) with possible follow-on testing in mammalian cells.**
  - **Test for mutagenicity and aquatic toxicity.**
- ***in vivo* testing for high potential MDA alt.**
  - **Performed in one species, usually rats.**
  - **Acute and chronic oral or inhalation toxicity testing, dermal and ocular sensitivity testing, mutagenicity, developmental or reproductive testing, and carcinogenicity testing.**

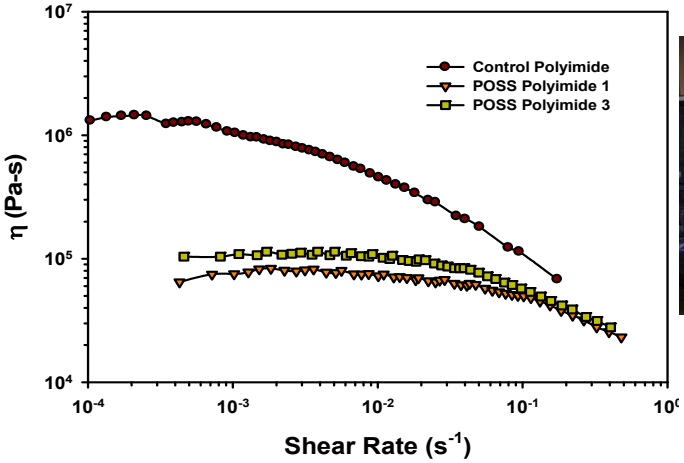


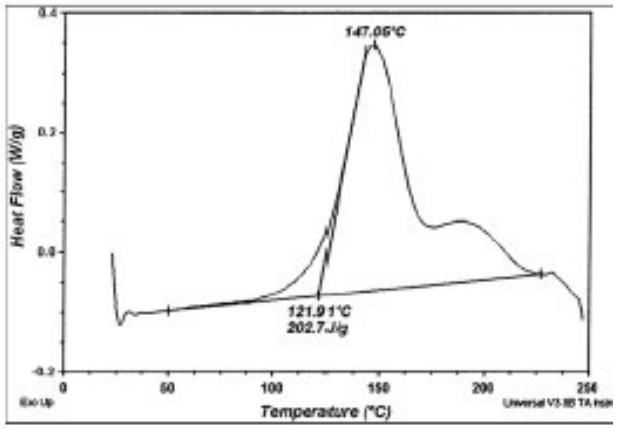


Resin Processing and Cure

- Dissolve NE, BTDE, and MDA alternative in methanol (ethanol as well to replace HAPs).
  - Assess solubility
- Reactions and analysis
  - Rheology – processing, MW
  - SEC – M_n, M_W, PDI
  - NMR, FTIR – confirm rxns, M_n
- Heats of Reaction







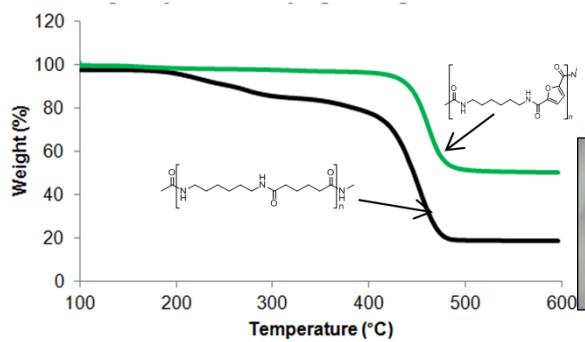
Metrics vs. PMR-15:
- Similar extent of amic acid olig.
- Imidization extent within 10%
- Amide and imide viscosity within 25%
- Heat of reaction per mole of amine no less than 95%
- Cure temperature no greater +25ºC

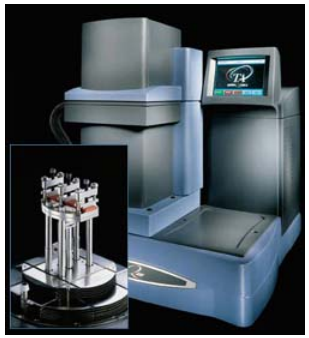
Neat Resin Properties

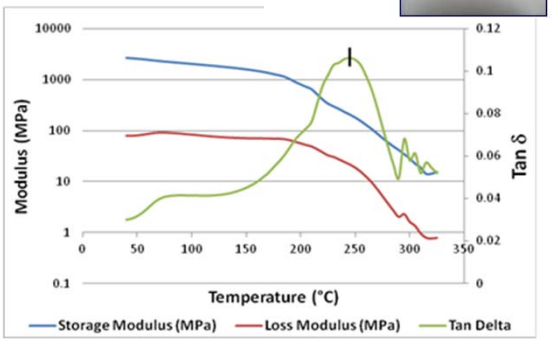
1. Prepare neat samples in steel blocks charged with dried imidized powder under pressure/heat
2. Thermogravimetric analysis to measure degradation temperature (T_d) (>400ºC)
3. Dynamic mechanical analysis to measure Tg (> 95% of 340ºC) and crosslink density

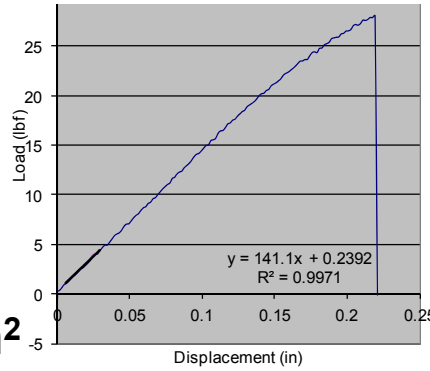
---

4. Thermoxidative stability
   - ~1wt% loss (500 h, 288°C), 5% loss (500 h, 316°C)
   - Retain flexural modulus >3.5 GPa flexural strength >150 MPa (ASTM D638)
5. ASTM D5045 Toughness > 250 J/m^2
6. Water absorption (95% RH, 71ºC) < 5 wt%



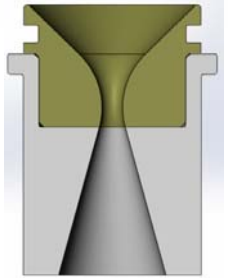




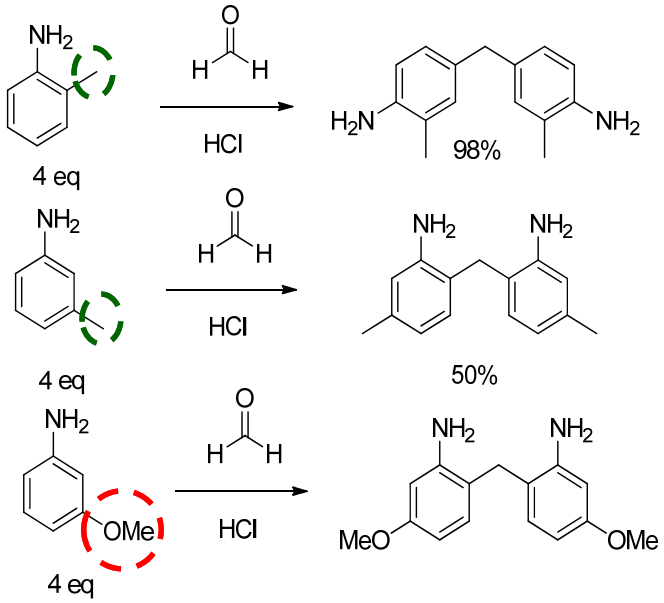


Composites and LCA

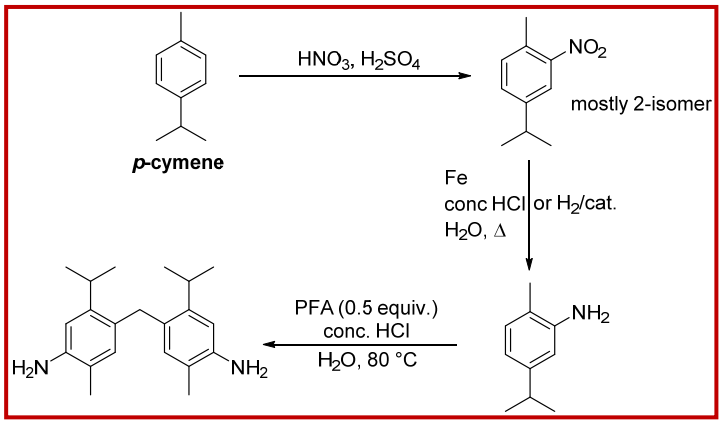
- AFRL to pre-preg carbon and glass fiber with input from Lockheed Martin Skunk Works (LMSW).
- Evaluate properties of carbon and glass fiber composites
  - Mechanicals
  - Water uptake
  - Thermo-oxidative exposure
- Proof of Concept Parts
  - Rocket casings (AFRL) and nozzles (AFRL/AMRDEC)
- LCA
  - Price of MDA alternatives
  - Cost savings due to reduced toxicity



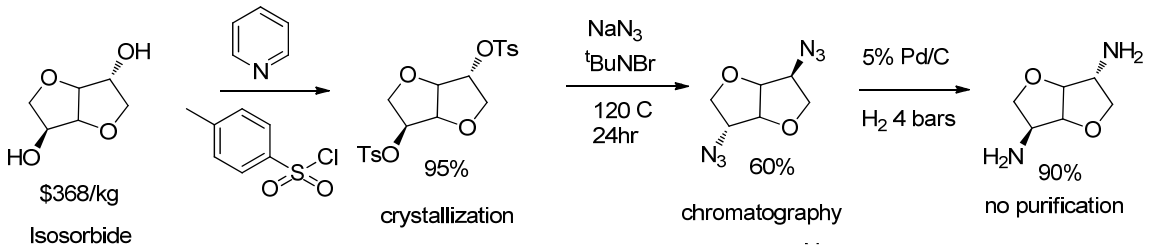
Overview of Prior Work – Synthesis

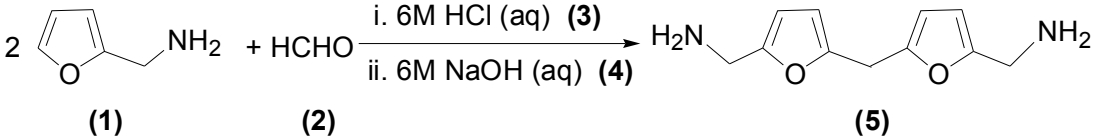


- **Prepared variants of MDA with multiple substituents on the rings**



- **Prepared variants of MDA with single substituents on the rings**

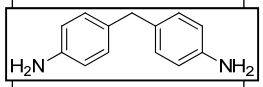
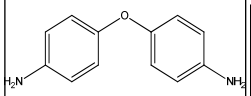
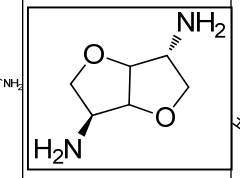
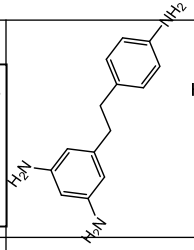
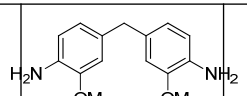
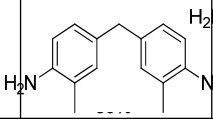
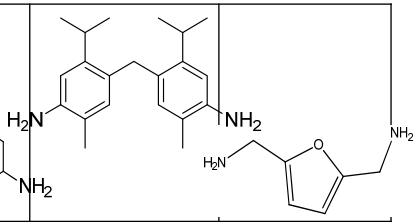


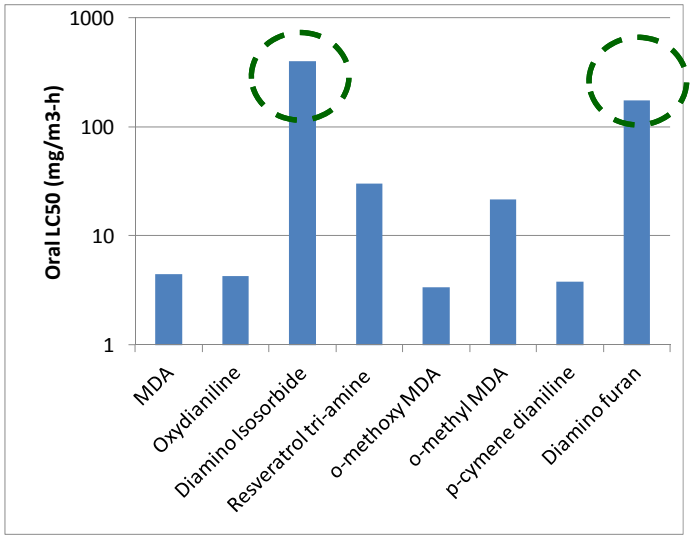


- **Prepared MDA variants with different ring chemistry in low yield**

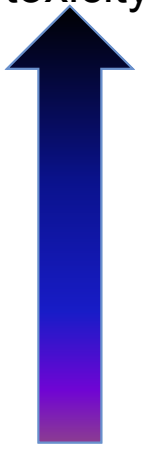
- **Prepared various potential diamines for structure-property-toxicity studies**

Overview of Prior Work – Toxicity

Structure								
Compound	MDA	Oxydianiline	Diamino Isosorbide	Resveratrol tri-amine	o-methoxy MDA	o-methyl MDA	p-cymene dianiline	Diamino furan
Mutagen	**Positive (DB value)**	**Positive (DB value)**	**Positive (High)**	**Positive (High)**	**Positive (High)**	Possible (High)	Indeterm	**Negative (Low)**
Carcinogen	**Positive (DB value)**	**Positive (DB value)**	Indeterm	Indeterm	Indeterm	Indeterm	Indeterm	**Unlikely**



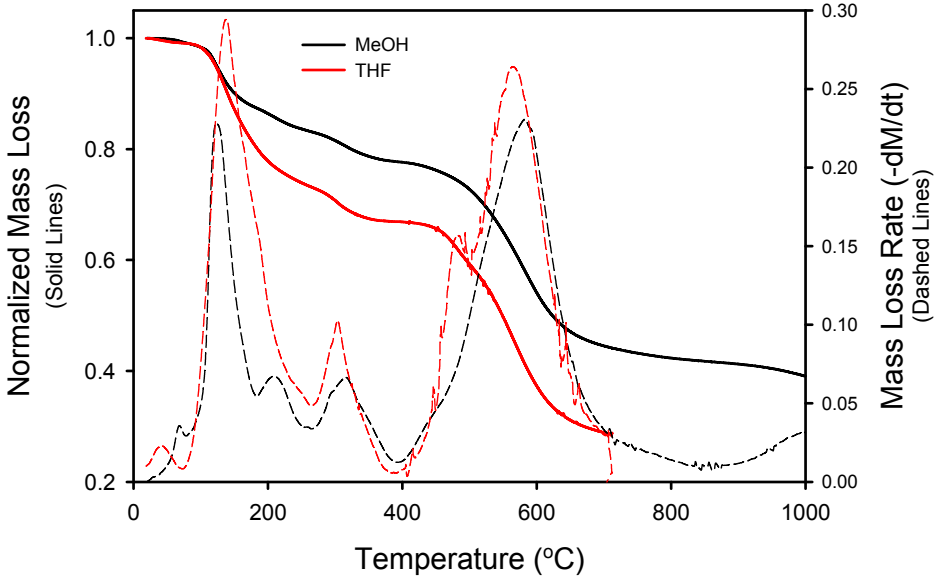
Reduced toxicity



- **QSAR results show that some non-phenyl amines have potential for low toxicity**
- **QSAR modeling completed on 25 compounds**

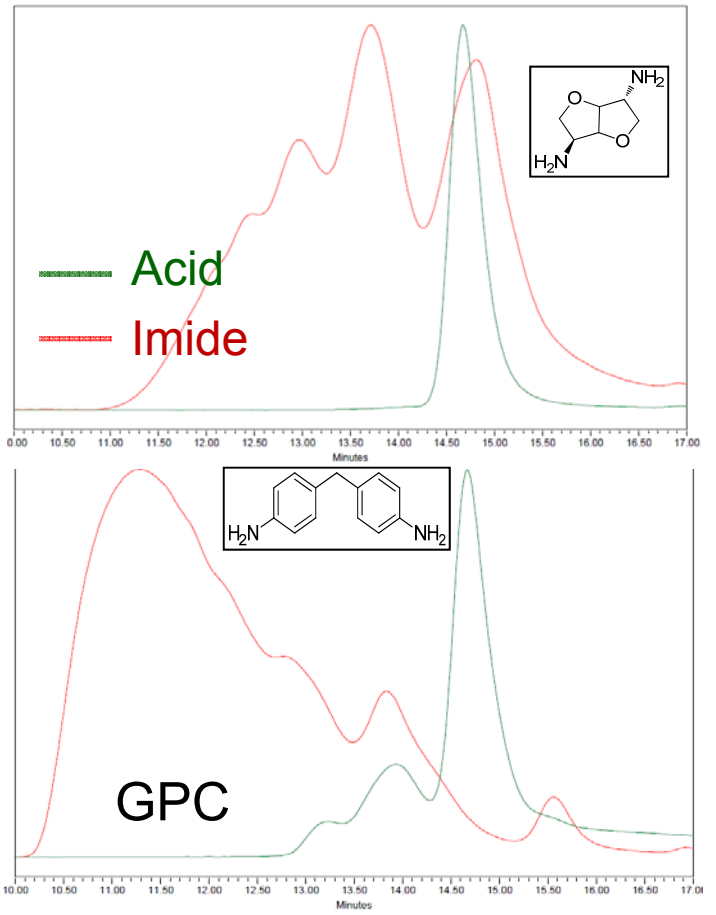
Overview of Prior Work – Processing/Polymerization

- **THF synthesis/processing of polyimides investigated to enable use of chemicals not soluble in methanol**

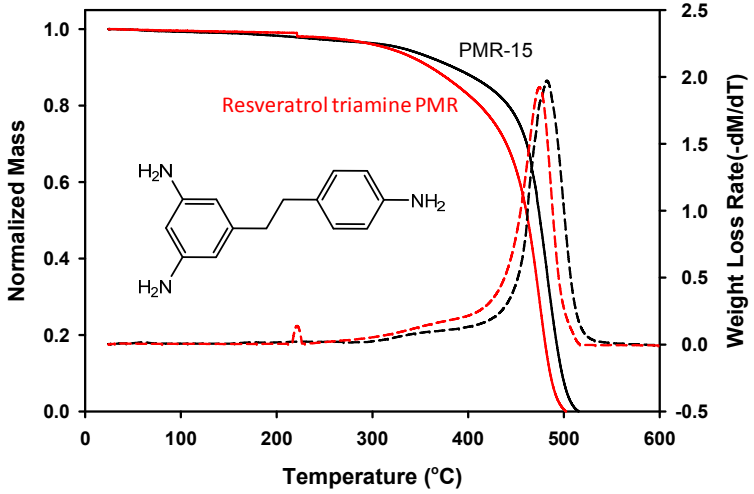


  - NE incorporated less in polyimide
  - Consistently yielded oligomers of higher average MW and PI
  - Higher MW oligomers have less crosslinkable endcap / reflected in TGA

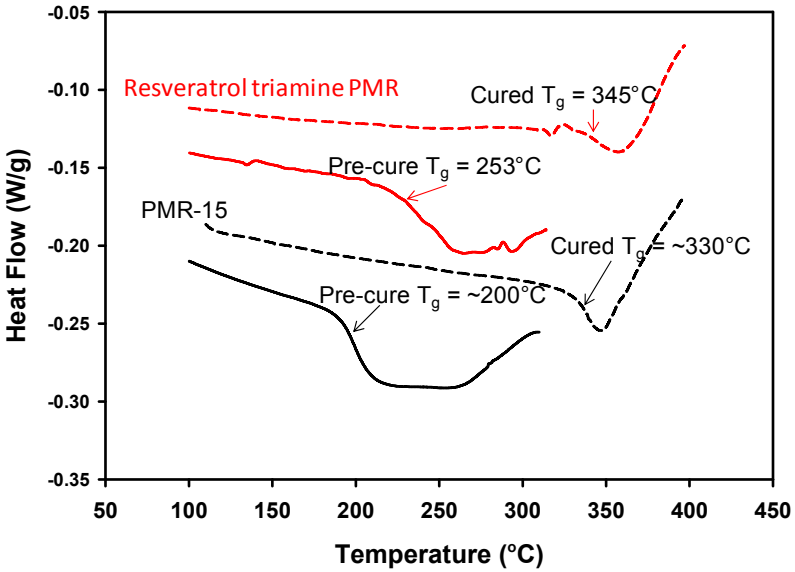
- **Monomer choice can affect polyamic acid MW and polyimide MW**

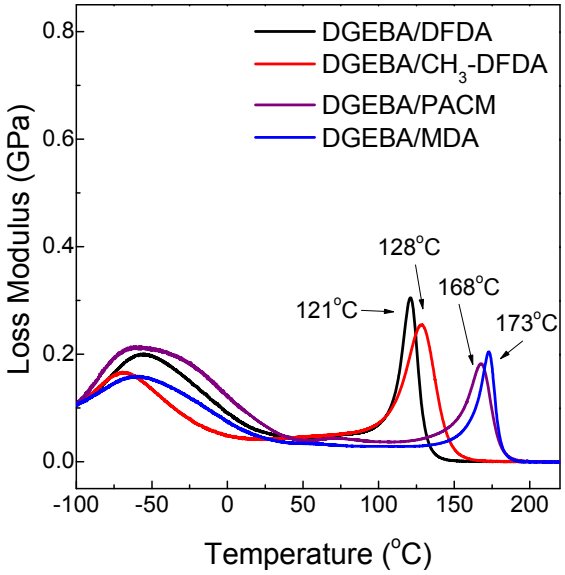


Overview of Prior Work – Polymer/Composites Properties



- Validated polymer testing methods
- Resveratrol polyimides with high thermal properties
- Furan-epoxy polymers with high char content but reduced T_g
- High quality polyimide composites (<1% void, 2.5 wt%loss at 316ºC for 410 h)





Prior Go/No Go Decisions

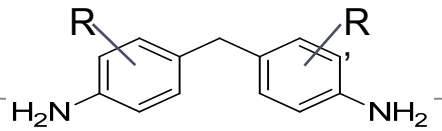
- Determine the feasibility of chemically preparing these MDA alternatives
  - ♦ Go – Chemical methods to prepare MDA alternatives are feasible and scalable

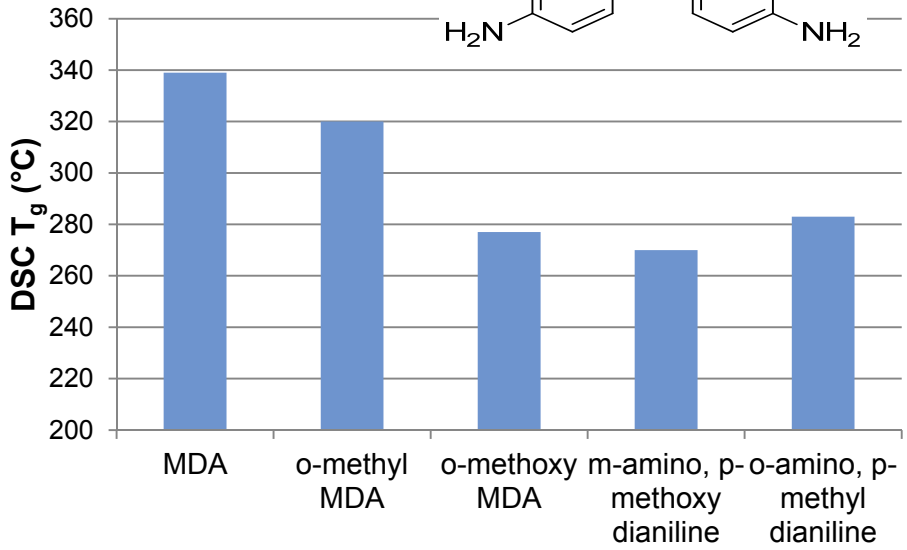
- QSARs indicate there are MDA alternatives with reduced toxicity
  - ♦ Go – QSAR suggests a number of compounds with reduced toxicity

Results – MDA Alternatives with Single Substituent

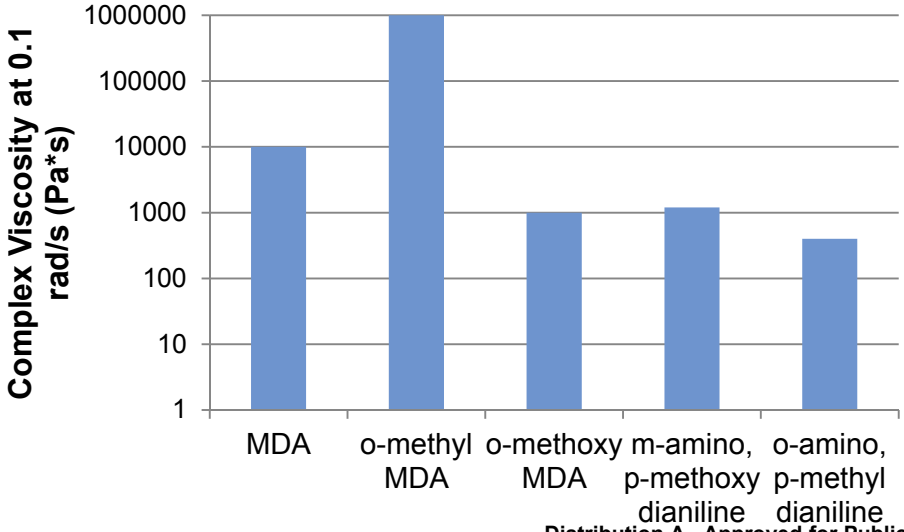
- **Ames Test—All are mutagenic**

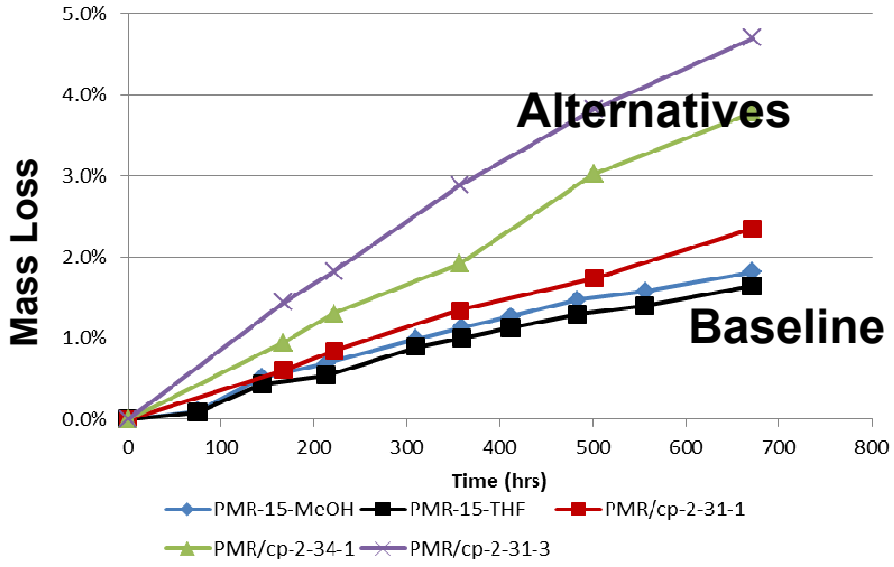
Compound	Microtox (aquatic) mg/L	NRU (acute toxicity) mg/kg
o-methoxy MDA	6.28 (moderate)	781 (very low)
o-amino, p-methyl MDA	42.3 (low)	684 (very low)



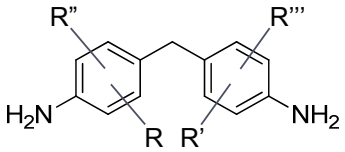


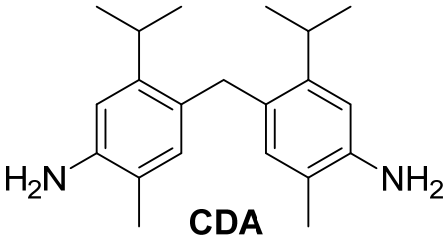
- **Viscosity varies around MDA**
- **T_g is generally reduced**
- **Mass loss is increased**





Results – p-Cymene Diamines





CDA

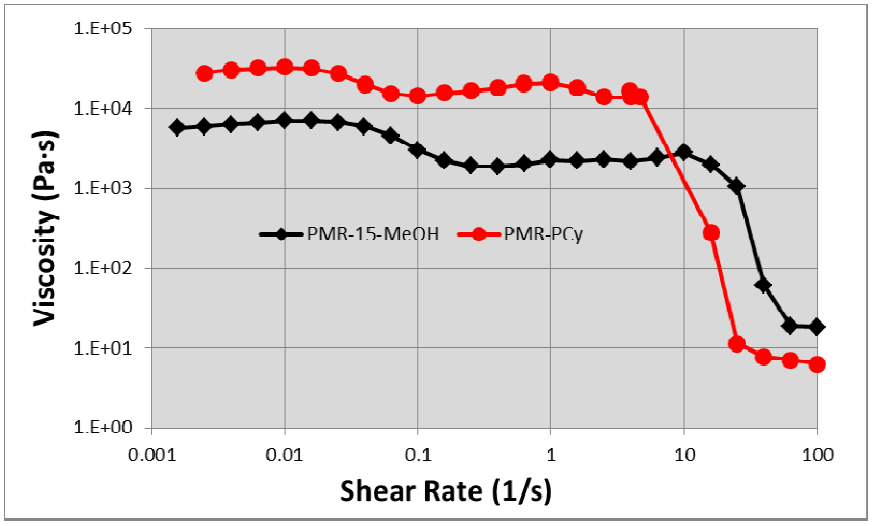
Toxicity

- Ames Test—no mutations for any of the strains tested
- Conclusion: not mutagenic or carcinogenic
- LD50: 725 mg/kg (very low tox.)
- Aquatic toxicity EC50: 299.3(1.3) mg/L (non-toxic)
- QSAR shows that all 11 isomers have low oral tox, but have elevated aquatic tox, mitigated by low solubility

Economics

- Turpentine produced at ~350 kton/y at $0.15/lb
- Limonene produced at 85 kton/y
- $0.4-3.0/lb on Alibaba for p-cymene
- Should eventually be low cost

Processing

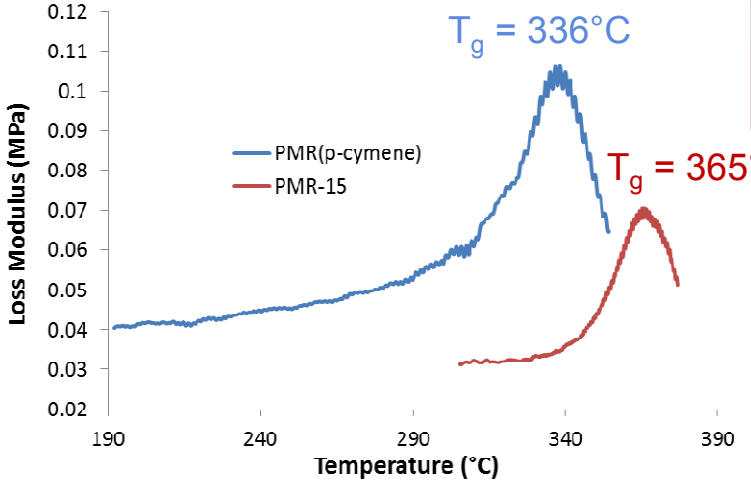


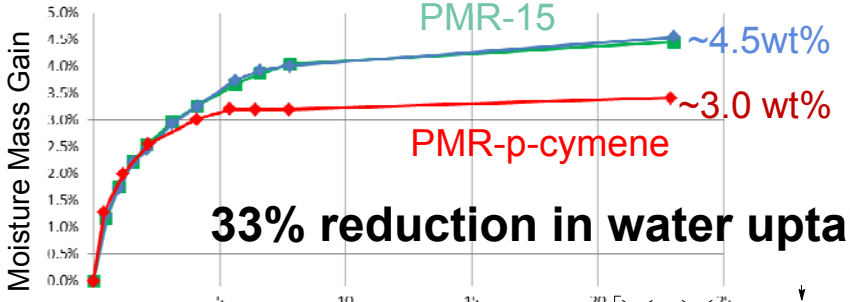
- PMR-PCy has similar viscosity/processing conditions relative to PMR-15
- Current efforts are focused on fabricating flat panels with PMR-PCy using cure protocols and processing parameters developed for PMR-15.

Results – p-Cymene Polyimides and Epoxies

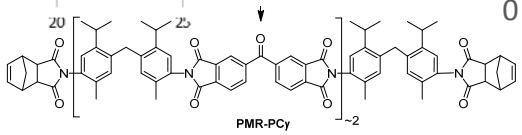
PMR Polyimides

- Lower T_g observed for PMR-PCy via both DSC and TMA (loss peak), but within 0.5-4.5% of PMR-15



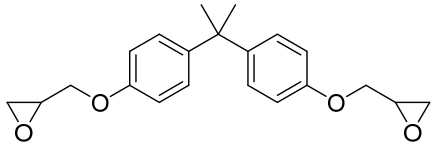


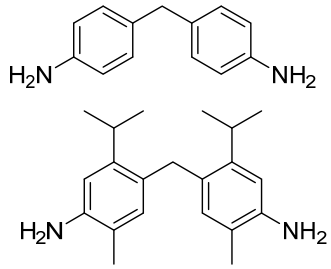
33% reduction in water uptake

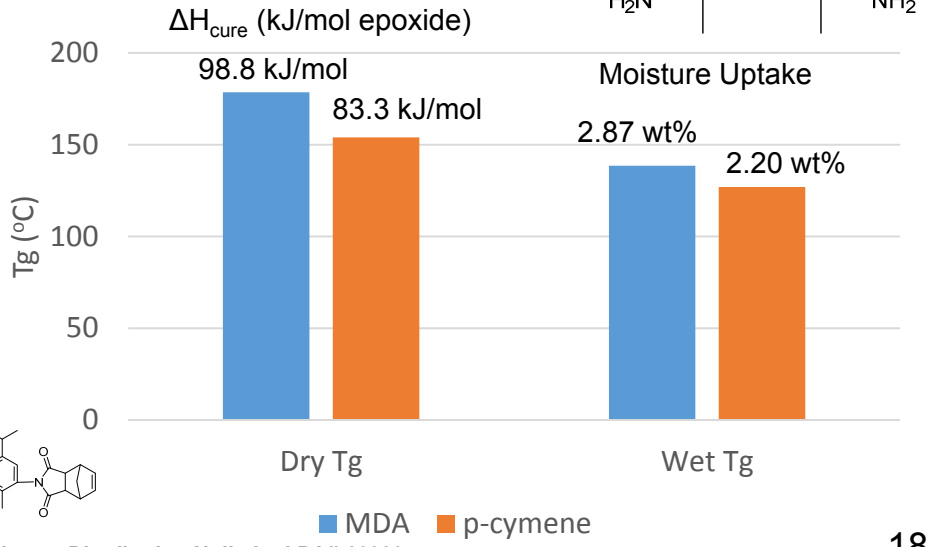


Epoxy-Amines

- Methyl and isopropyl groups on amine result in 18-24ºC drop in T_g (DSC and TMA) likely due to reduced extent of cure
- 0.4-0.6 wt% (23%) reduction in water uptake
- Similar T_d (~370ºC)

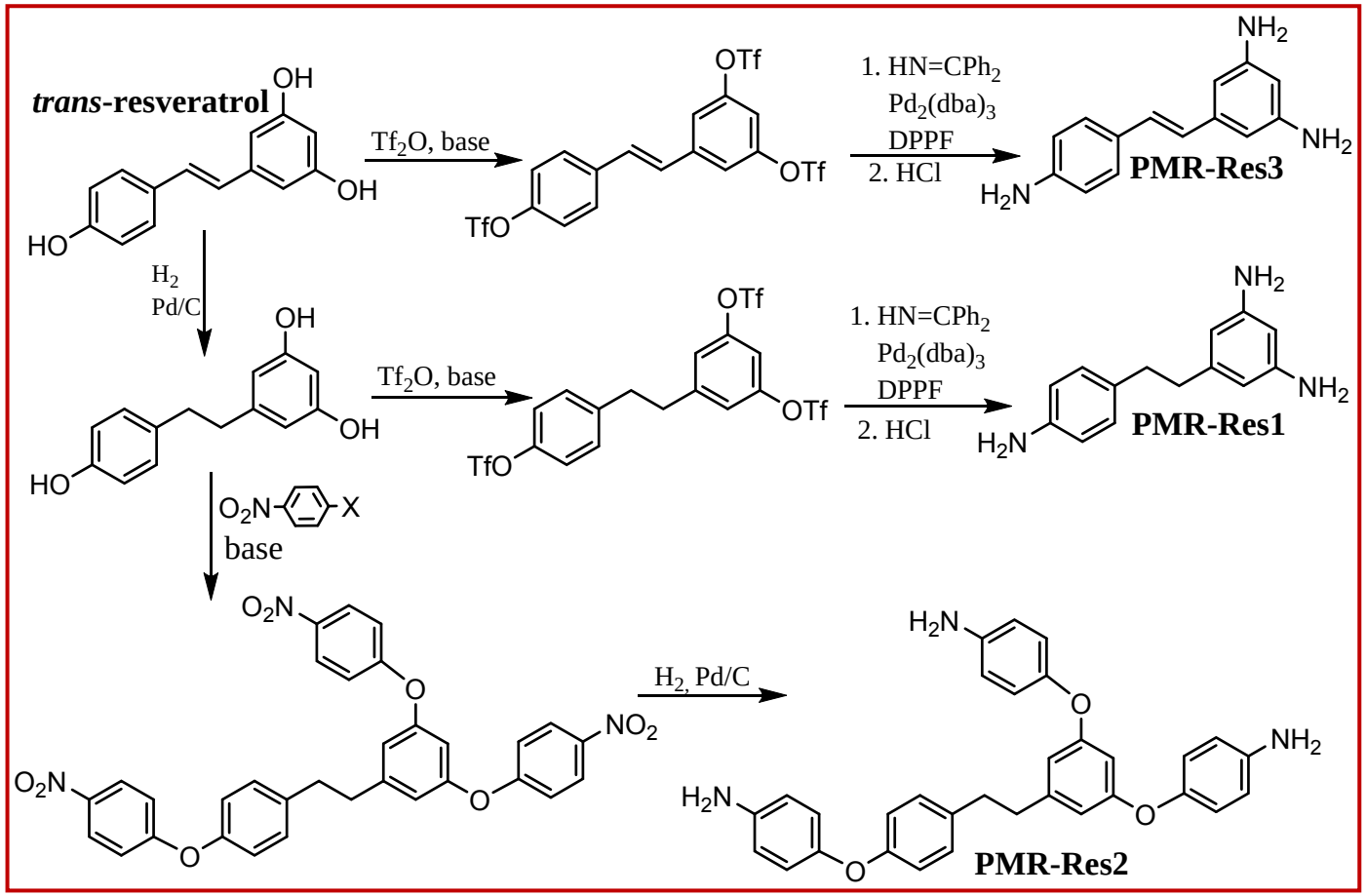






Results – Tris(Aniline) Monomers

- **Resveratrol can be generated biosynthetically from sugars.**
- **Starting trisphenol is conducted in water with low energy demands.**
- **No formaldehyde or other toxic chemicals are used in the process.**



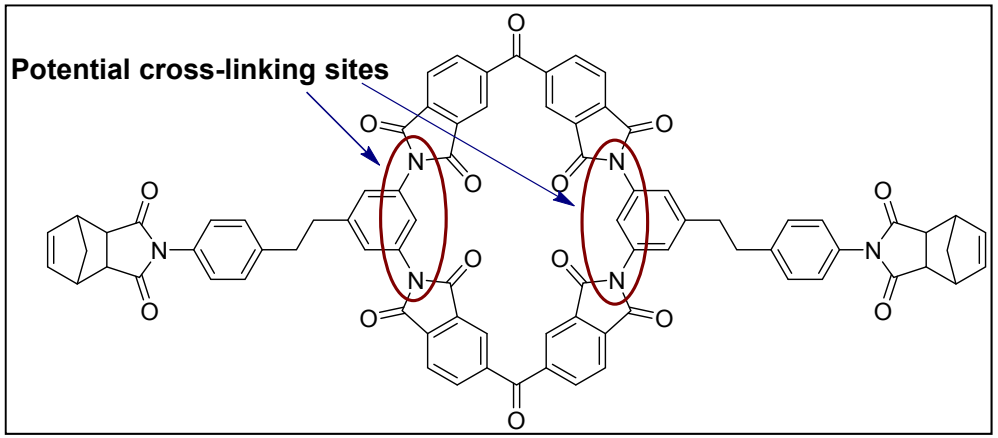
Mutagenic
Cytotoxic >/= 3.2 µg/mL

Mutagenic
Cytotoxic >/= 3.2 µg/mL

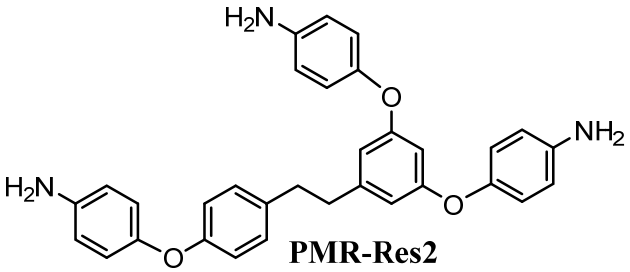
<u>Not</u> Mutagenic based on AMES testing
No cytotoxicity observes up to solubility limit of 10 µg/mL

Results – Tris(Aniline) Polyimides

Processing

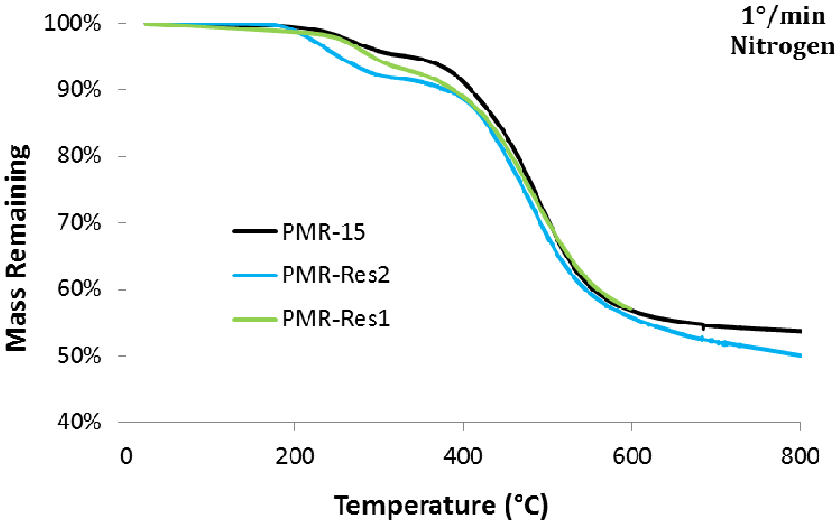


- Trisanilines can cross-link during polyamic acid formation leading to insoluble oligomers.
- Current efforts: Optimize rxn time during formation of the amic acids

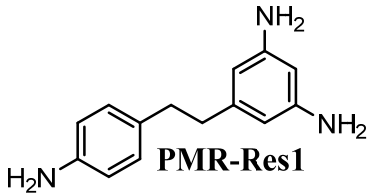


Not optimized T_g = 324 °C (DSC)

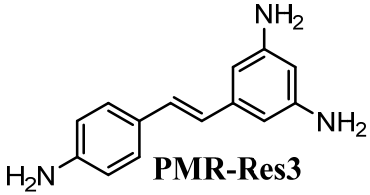
Polymer Properties



- Higher Tg than MDA is possible
- Similar thermal degradation results (TGA)
- Future efforts: TOS

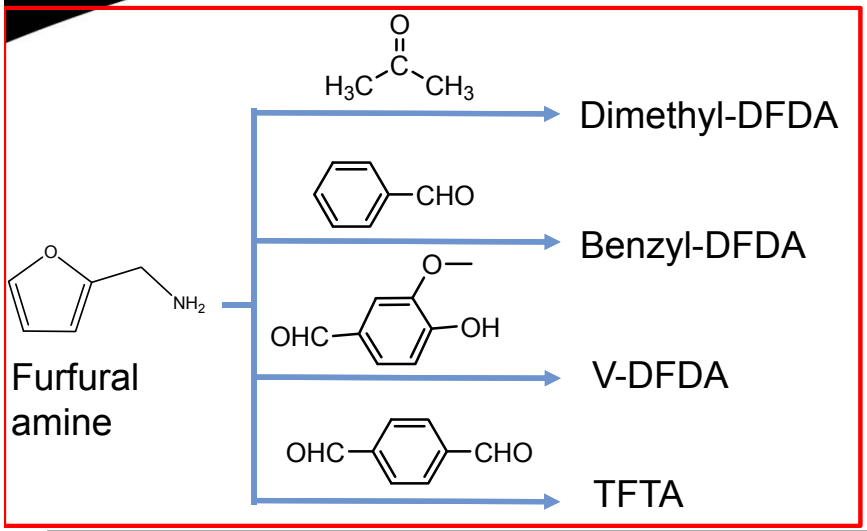


T_g = 347 °C (DSC)

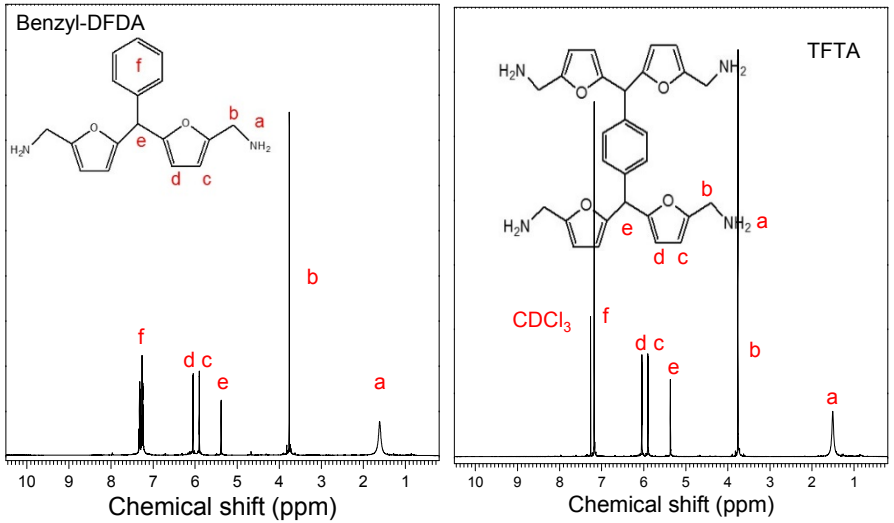


Uncured T_g = 265 °C
Postcure T_g = ???

Results: Furan-Based Diamine Synthesis



Amines	Purity (^{1}H-NMR)	Amine/ aldehyde ratio	Temp.	Time
DFDA	99%	1:2	25 °C	70 min
CH_3-DFDA	98%	1:2	40 °C	70 min
DM-DFDA	97%	1:2	40 °C	24 h
Benzyl-DFDA	99%	1:10	40 °C	24 h
TFTA	99%	1:20	40 °C	24 h
V-DFDA	99%	1:10	40 °C	24 h



^{1}H-NMR spectra of furan based amines

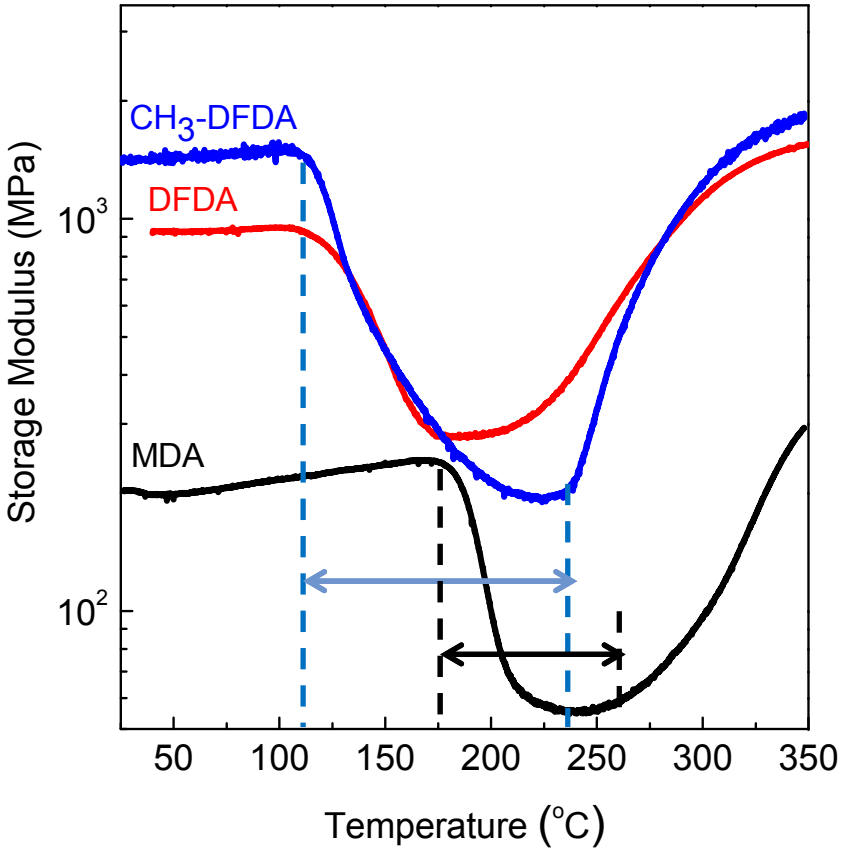
Toxicity

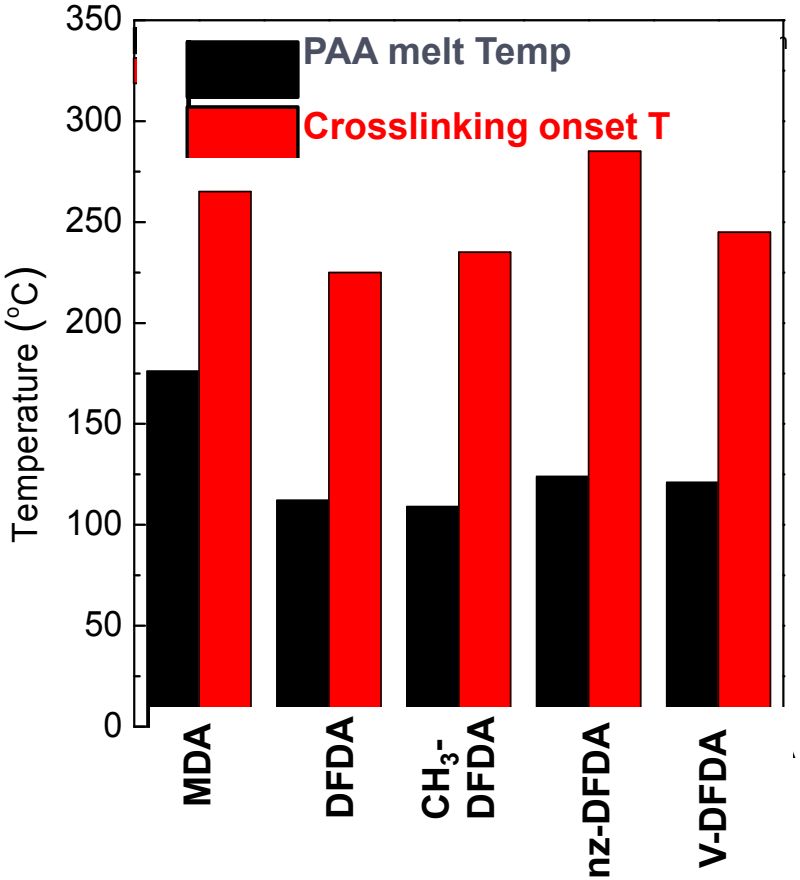
- **QSAR – predicted low toxicity for all R and R'**
- **Not Mutagenic based on AMES testing**
- **No cytotoxicity observed up to solubility limit of 10 μg/mL**

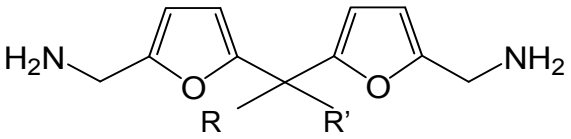
- **One-step** synthesis method with high purity.
- Benzyl-DFDA, V-DFDA and TFTA are combinations of phenyl and furfural building blocks.
- A wide variety of bio-based aldehydes can be used to prepare furan based amines .

Result: Prepared various novel furan based diamines for PMR synthesis.

Results – Furan Polyimides Processing

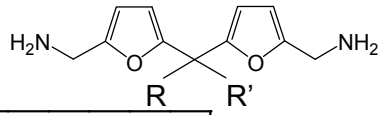




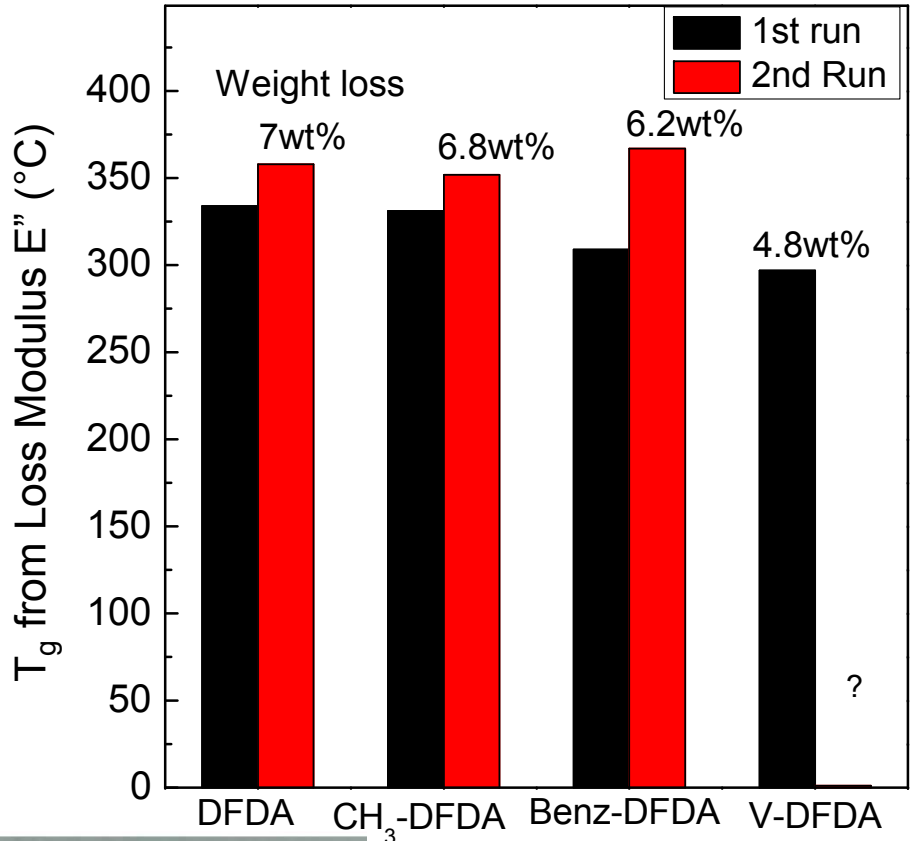


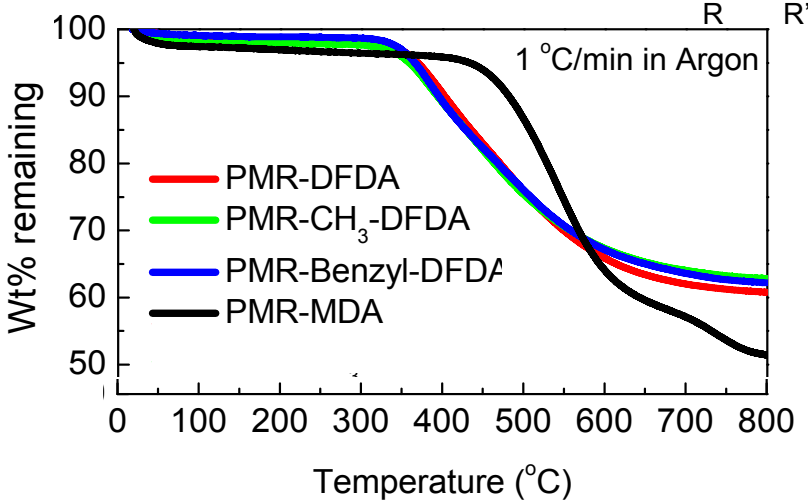
- **Lower polyamic acid melt temperature for furans**
- **Lower curing temperature for furans**

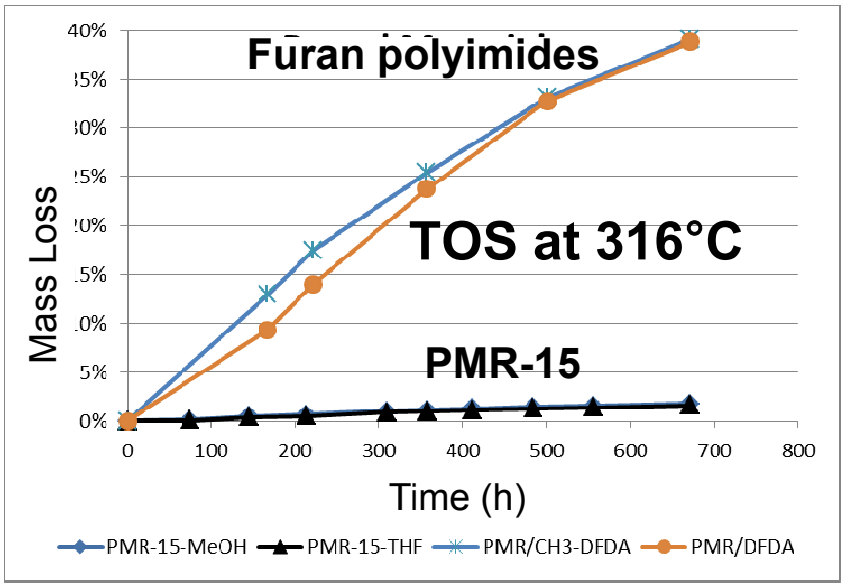
Results – Furan Polyimide Polymers



T_g(E") = 365°C for PMR-15

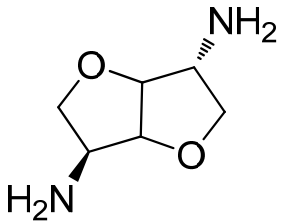






- **Furan polyimides can have high T_g**
- **TOS is an issue at very high temperatures**

Results – Diamino Isosorbide

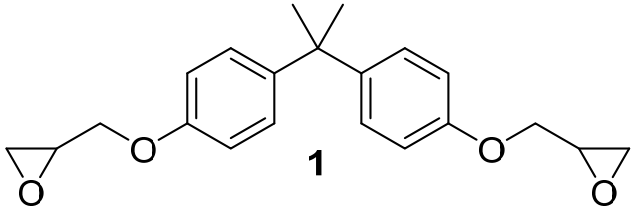


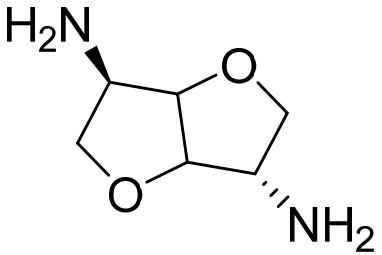
Toxicity

- **Ames Test—no mutations for any of the strains tested**
- **Conclusion: not mutagenic or carcinogenic**
- **LD50: >2000 mg/kg (not toxic)**
- **Aquatic toxicity EC50: 19.84(1.3) mg/L (low-toxicity)**

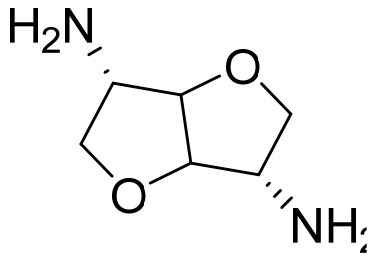
- **Previous results showed poor polyamic acid formation**
- **Polyimide T_g = 240° C**

Diamine	ΔH_{rxn} (kJ/mol)	Normalized ΔH_{rxn}
MDA	373	1
Diamino isosorbide	0	0
Diamino isomannide	315	0.84





Diamino isosorbide



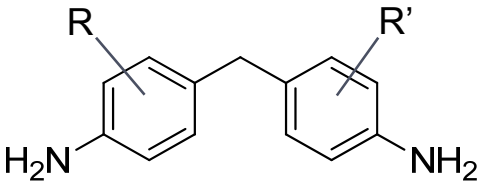
Diamino isomannide

- **Stereochemistry of isosorbide prevents its utility as a diamine curing agent**

Results – Structure-Property-Toxicity

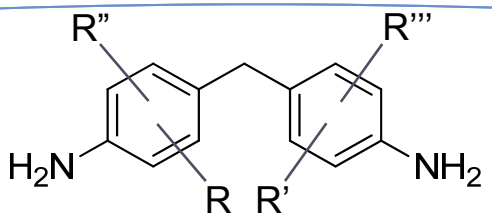
Positives

- Inexpensive reactants

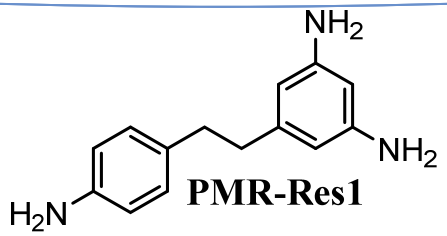


- High toxicity

- Low toxicity
- High thermal properties

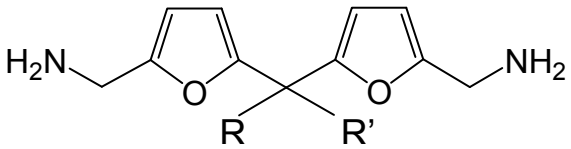


- Can have improved thermal properties



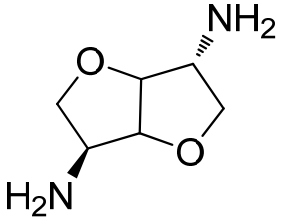
- More difficulty in processing (crosslinking)
- Relatively expensive reactants (currently)

- Low toxicity
- Improved processing
- Reasonable thermal properties



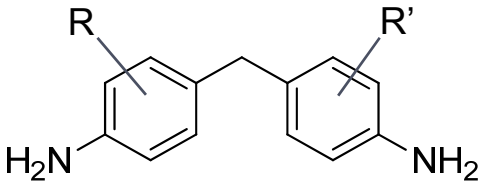
- Reduced TOS

- Low toxicity

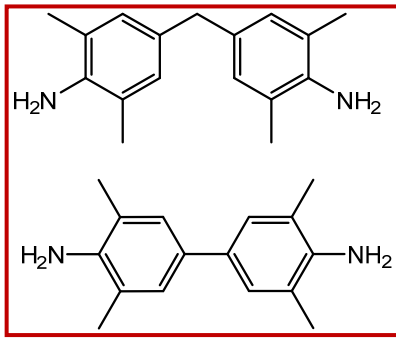


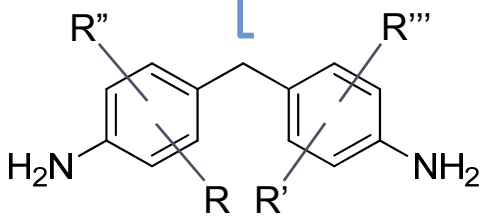
- Low polymer properties (poor reactivity)

Gaps/Work to Complete

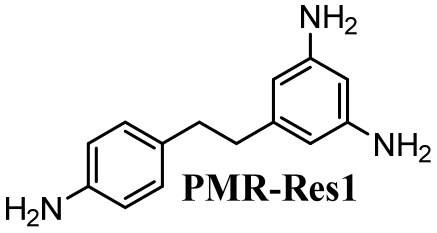


- No go as MDA alternative
- Polyimide and epoxy papers

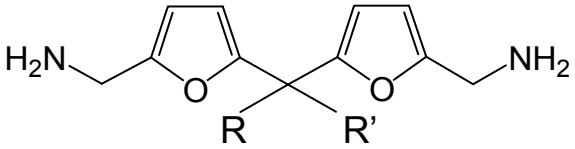




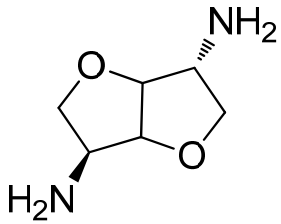
- Do two substituents reduce toxicity or do two specific substituents reduce toxicity?
  - Additional monomers/polymers to address this gap
- Polyimide papers
- Polyimide composites



- Optimize polyamic acid formation
- Polyimide composites only using PMR-Res2
- TOS studies



- Paper on how substituents affect properties
- Polyimide composites for lower temp applications

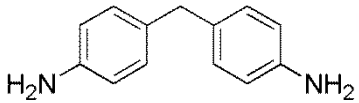


- No go as MDA alternative
- Very low priority – identify catalyst to enable facile polyamic acid and polyimide formation
- Report in above papers

Summary and Conclusions

- Identified a number of non-toxic diamines.
- QSAR indicates that all diamines evaluated had minimal endocrine disruption. (H. Hong et al., FDA leveraging)
- Multi-substituents on phenolic ring results in low toxicity, good processing, and high properties.
- Some gaps remain in structure-property-toxicity studies
- Move forward with scale-up and composites evaluations of promising formulations

Problem Statement



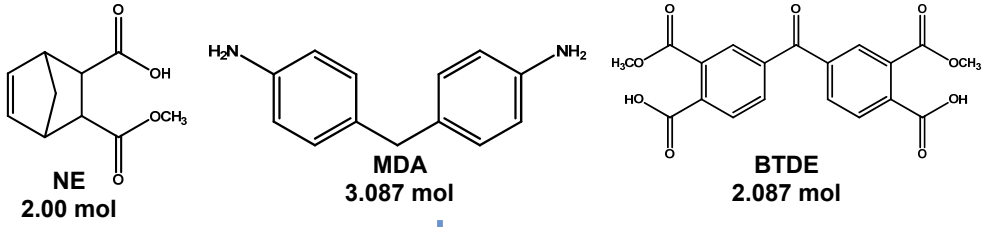
- **4,4'-methylene dianiline (MDA) is a liver toxin and carcinogen.**
- **PMR-15 uses MDA (Monsanto Skybond 701 and LARC-Si as well)**
  - **Usage: ~20,000 lbs/yr PMR-15 – almost all for DoD applications.**
  - **Aircraft engines, rocket casings, engine bypass ducts, nozzle flaps, bushings, bearings, missile fins, structural wing components, radar domes, and other DoD applications requiring high temperature composites.**
  - **Largest use: Outer Bypass Duct of GE Aviation's F/A-18E/F & EA-18G engines.**
  - **Most versatile polyimide – Excellent balance of processing, mechanical, and thermal properties**

- **Toxicity poses added cost to government in increased production costs and decreased competition.**
- **EPA Composite Manufacturing and Repair National Emission Standard for Hazardous Air Pollutants regulations, Army Environmental Requirements and Technology Assessments, and REACH prohibit new use.**

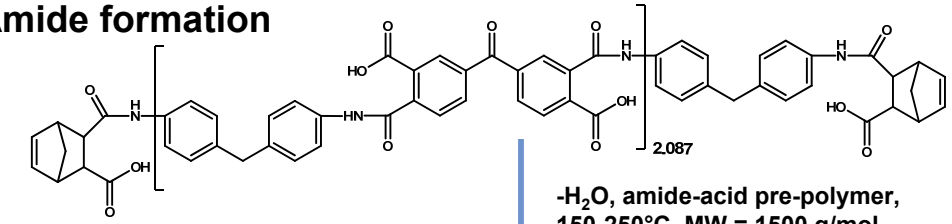
Technical Background – PMR-15

- **PMR-15 is *P*olymerization of the *M*onomer *R*eactants MDA, 5-norbornene-2,3´-dicarboxylic half acid ester (NE), and 3,3´,4,4´-benzophenonetetracarboxylic diester (BTDE)**

Solids

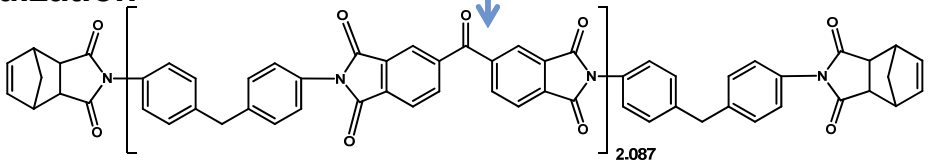


Amide formation



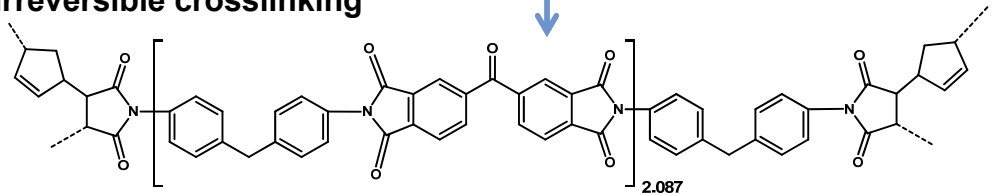
-H_2O, amide-acid pre-polymer, 150-250°C, MW = 1500 g/mol

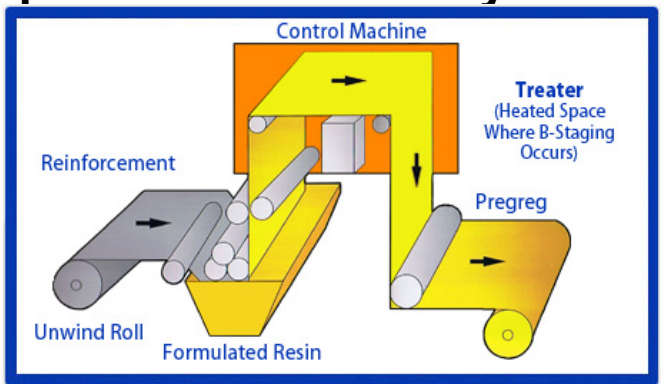
Imidization

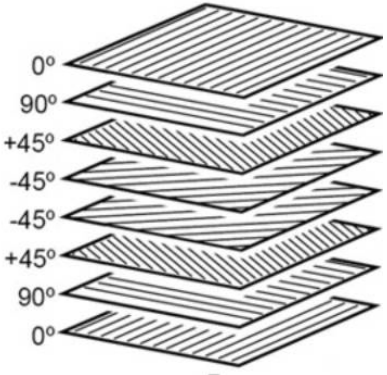


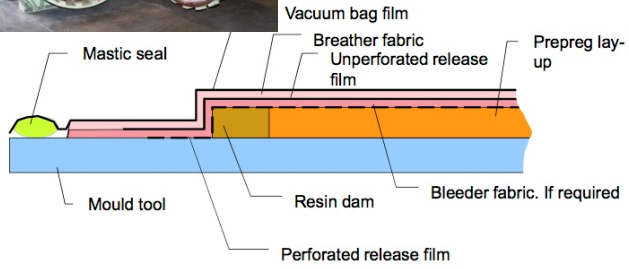
Pressure, 250-216°C

Reverse Diels Alder irreversible crosslinking



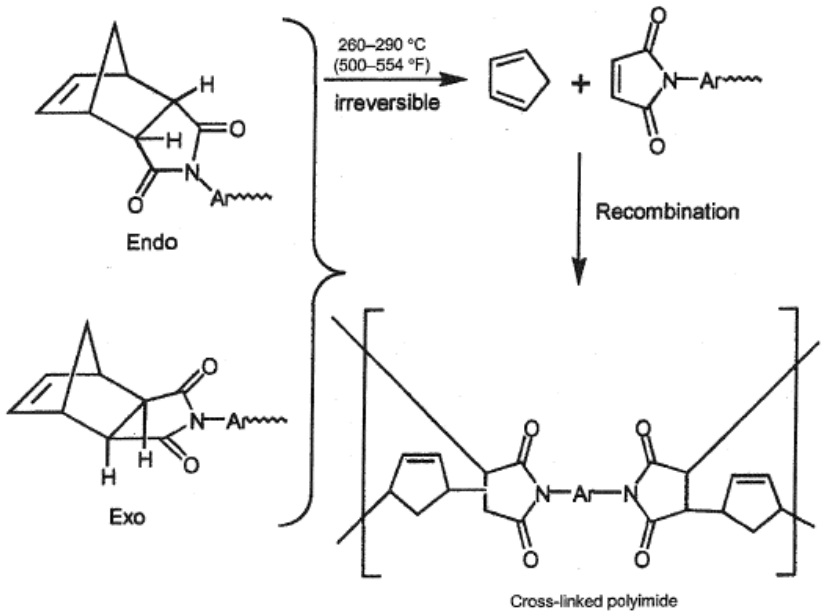




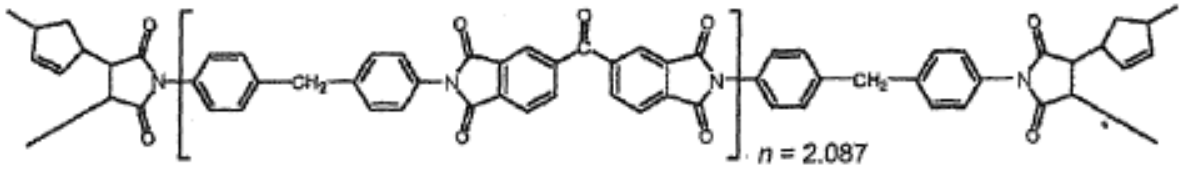


Technical Background – PMR-15

- **Reverse Diels Alder irreversible crosslinking**



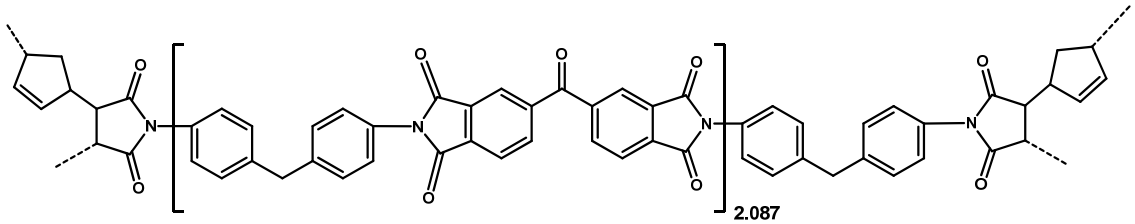
- **Highly aromatic, sp^2 planar bonded structure**
  - **Results in high glass transition temperature and degradation temperature**
- **Exceptions to sp^2 structure:**
  - **Methylene bridge between the phenyl units in MDA and the crosslinking of the NE**
  - **Provides toughness**



Thermally cross-linked polyimide

Technical Background – Properties

- Highly aromatic, sp^2 planar bonded structure results in high glass transition temperature (T_g) and degradation temperature (T_d)
- Exceptions to sp^2 structure provide toughness and improved processability



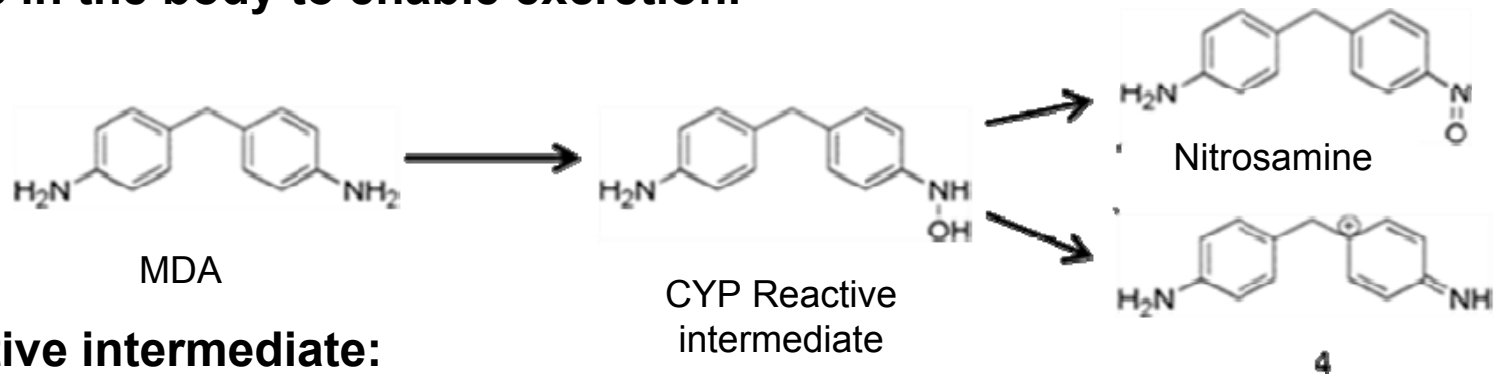
Neat resin properties

Property	Modulus (GPa)	Strength (MPa)	Elongation (%)
Flexural	4.0	~175	1.5
Tensile	3.9	~40	1.1

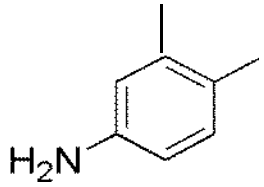
- Fracture toughness ~280 J/m^2
- Water absorption at 95% RH and 71°C = 4.2%
- Tg = 340°C (320°C after 1 h at 316°C)
- Weight loss under flowing air:
  - ~1% (500 h, 288°C)
  - ~5% (500 h, 316°C)
- Other polyimides can have higher glass transition temperature (T_g), strength, toughness, ***OR*** degradation temperature, but PMR-15 has highest aggregate of these properties.

Technical Background – MDA Toxicity

- **Liver uses cytochrome P450 (CYP) enzyme to oxidize organic chemicals in the body to enable excretion.**



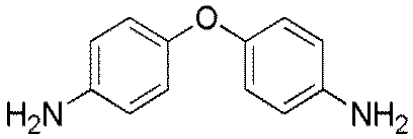
- **CYP reactive intermediate:**
  - **Is highly reactive and damages liver tissue.**
  - **Readily yields carcinogenic nitrosamine.**
- **A.G. Siraki, et al., "N-oxidation of aromatic amines by intracellular oxidases."** ***Drug Metab Rev.,*** **2002, 34, 549-564.**
  - **The reactivity of CYP towards a chemical is based on the chemical's functional groups, shape, and size.**



- **Changes in the electronics of the aromatic ring should yield derivatives with lower reactivity towards metabolizing enzymes resulting and affect solubility in reduced toxicity.**

Technical Background –
MDA Alternatives

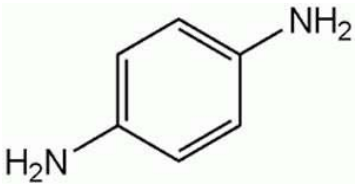
- **Other diamine monomers have been studied and used.**



4,4'-oxydianiline

Kapton, LARC PDMDA, Amoco Ultradel 4212, Mitsui-Tuatso TPI Aurum, 6F Pyralin, LARC RP-46

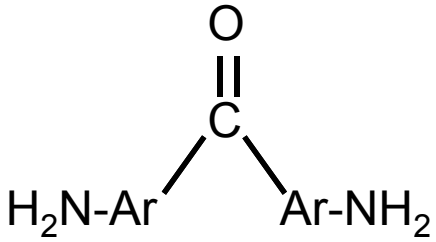
Phenylene diamine



AFR 700B, VCAP-II, Superimide 800

$H_2N\text{-}Ar\text{—}Ar\text{-}NH_2$

Amoco Ultradel 4212, Mitsui-Tuatso TPI Aurum



LARC-TPI

- **4,4'-oxydianiline reduces toxicity (but is still toxic), *but also* thermal stability.** R.H. Pater, "Thermosetting polyimides: a review." *SAMPE J.*, 1994, **30**, 29–38.
- **Other alternatives are just as toxic as MDA (but used less) and affect polymer properties.**

Technical Background

MDA Alternatives – Technical Gaps

- **No systematic approach to monomer architecture and its effect on toxicity.**
- **No consideration of non-phenyl aromatic groups, such as furans, and non-aromatic cyclic groups, such as isosorbide, as units of the PMR monomers to reduce toxicity and rigidize the resulting polymer.**

Toxicity Assessment

- **ESOH toxicity assessment performed in accordance with ASTM Guide E2552 and USAPHC Standing Operating Procedures.**
- **Toxicity testing conducted in a phased manner, according to the level of item development.**
  - **Quicker, less expensive testing done initially**
  - **More definitive, costly testing done on best candidate(s)**